



Serial No. 09/414,526
SEC.637

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent application of :
Yeong-Kwan Kim et al. : Group Art Unit 1762
Serial No. 09/414,526 : Examiner Michael Cleveland
Filed October 8, 1999 :
METHOD FOR MANUFACTURING THIN FILM

APPELLANT'S BRIEF

Honorable Commissioner For Patents
Washington, D.C. 20231

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Sir:

Pursuant to the provisions of 37 C.F.R. ¶1.192, this Appellant's Brief is respectfully submitted (in triplicate) subsequent to the filing of a Notice of Appeal on August 5, 2003.

I. REAL PARTY IN INTEREST

The real party in interest is the assignee of the application, i.e., SAMSUNG ELECTRONICS CO., LTD., headquartered in the Republic of Korea.

II. RELATED APPEALS AND INTERFERENCES

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There are no other appeals or interferences known to the appellant, the appellant's legal representative, or assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in this pending appeal.

III. STATUS OF CLAIMS

Originally presented claims 1-14 have been canceled, and claims 15-27 are pending in the application.

Claims 20 and 26 have been withdrawn from consideration as being directed to non-elected species, and the remaining claims 15-19, 21-25 and 27 and are the claims appealed.

IV. STATUS OF AMENDMENTS

No amendments have been filed subsequent to the final rejection of May 9, 2003.

V. SUMMARY OF INVENTION

As described in the Background section of the present application, there are a number of known methods for depositing a thin dielectric layer in which a reactant is periodically supplied to the surface of a substrate. It has been found,

however, that these methods generally result in defects at the interface between the film and substrate, and in defects in the film itself. The invention of the appealed claims is particularly directed to reducing film defects in the formation of an oxide film.

In particular, the present inventors have found that flushing the surface of the silicon substrate with oxygen atoms prior to growth of the oxide film enhances the oxide film characteristics. Fig. 2 of the application illustrates the results of the flushing process in which oxygen atoms O are bonded to the silicon Si of the substrate. (Spec., page 6, lines 10-17). The oxygen atoms function to replace impurities (which cause defects) at the substrate surface, such a carbon or nitrogen, due to the relatively strong oxygen-silicon bond. (Spec. page 6, line 18, through page 7, line 15.) The result is a homogeneous substrate surface that is uniformly terminated with oxygen atoms.

Further, to achieve decomposition of silicon and CH_3 radicals of the TMA, the substrate is heated to a temperature of 120 to 370 °C, preferably 300 °C, prior to the flushing process. (Spec., page 9, lines 14-16, and page 10, lines 7-10.)

The terminated oxygen atoms are used in a reaction process which follows the flushing process. For example, trimethylaluminum $\text{Al}(\text{CH}_3)_3$ (TMA) may constitute a first reactant which is introduced into the chamber. After purging of the chamber to remove any physically absorbed first reactant, a substrate results in

which the first reactant is chemically absorbed onto the oxygen terminated surface of the substrate. (Spec., page 8, lines 3-8.) As shown in Fig. 3, in the case of TMA, the chemically bonded first reactant exists in various forms such as Si-O-CH₃ radicals or Si-O-Al-CH₃ radicals. (Spec., page 8, lines 8-10.)

A second reactant is then introduced into the chamber, and as a result of chemical exchange or reaction with the first reactant, an oxide film is formed on the substrate. For example, Al₂O₃ and CH₄ are formed in the case where the first reactant is TMA and the second reactant is water H₂O. The CH₄ is removed by evaporation, and the result is a high quality oxide film formed on a silicon substrate, for example, an aluminum oxide film having a Si-O-Al-O structure. (Spec., page 8, lines 11-19.)

VI. ISSUES

The issues presented for review are (a) whether claims 15-18, 21-25 and 27 stand properly rejected under 35 U.S.C. §103 as being unpatentable over "Kim et al." (Appl. Phys. Lett., 71, pp. 3604-3606) in view of "Marcus et al." (U.S. Pat. No. 5169579) and "Luryi" (U.S. Pat. No. 4806996); and (b) whether claims 19 stands properly rejected under 35 U.S.C. §103 as being unpatentable over Kim et al. in view of Marcus et al., Luryi and "Comizzoli et al." (U.S. Pat. No. 5851849).

VII. GROUPING OF THE CLAIMS

In the context of this Appellants Brief only, claims 15-18, 21-25 and 27, are considered to stand or fall together.

VIII. ARGUMENT

A. 35 U.S.C. ¶103 – CLAIMS 15-18, 21-25 and 27

Claims 15-18, 21-25 and 27 stand finally rejected under 35 U.S.C. ¶103 as being unpatentable over Kim et al. in view of Marcus et al. and Luryi. However, Appellants respectfully contend that this rejection should be reversed.

Independent claim 15 recites a method in the surface of a substrate is flushed with oxygen within a reaction chamber so as to uniformly terminate dangling bonds on the surface of the substrate with oxygen atoms at a substrate temperature of 120 to 370 °C. A first reactant is then chemically absorbed onto the terminated surface of the substrate by introducing the first reactant into the reaction chamber. A film of an oxide material is then formed as a result of a chemical exchange or reaction of the chemically adsorbed first reactant and a second reactant by introducing the second reactant into the reaction chamber, where the oxide material includes of the oxygen atoms used to terminate the surface of the substrate.

Appellants agree that Kim et al. teaches the sequential use of first and second reactants (TMA and water) to form an oxide film (aluminum oxide) on a silicon substrate.

Further, the Examiner acknowledges, and Appellants agree, that Kim et al. does not teach termination of the substrate surface with oxygen, and that instead the surface of the substrate of Kim et al. is terminated with hydrogen prior to formation of the Al_2O_3 films. However, the Examiner contends that it would be obvious to modify Kim et al. to terminate the substrate surface with oxygen instead of hydrogen in view of the teachings of Marcus et al. Appellants respectfully disagree.

***The atomic hydrogen termination of Kim et al. is a
by-product of a cleaning and etching process.***

The Examiner alleges that Kim et al. teach “cleaning to uniformly terminate the surface with atomic hydrogen”. The Examiner’s use of the word “uniformly” is curious, since it appears in the present claims but does not appear in the Kim et al. reference. In any event, the Examiner has failed to address the reasons given by Kim et al. for the cleaning of the wafer surface, and, perhaps more importantly, the manner in which Kim et al. cleans the wafer surface.

Specifically, Kim et al. reads as follows:

“Prior to the growth of the Al₂O₃ films, the native oxide covered substrate, Si(100), was cleaned by the conventional wet chemical treatment and diluted HF etching in sequence for the removal of particles and native oxides, respectively. The surface of Si wafer prepared in this manner is known to be contamination-free and terminated with atomic hydrogen.” (Emphasis added.)

Accordingly, the objective of the pretreatment of Kim et al. is to remove oxides. Further, the termination of the Si surface with atomic hydrogen is a by-product of the etching process using HF. It is not apparent to Appellants how Kim et al. might be modified to etch the surface of the silicon substrate to remove particles and oxides, such that the resultant surface is instead terminated with oxygen.

The Examiner states:

“Applicant argues that the objective of Kim is to “remove native oxides in the pretreatment [of the substrate]”. The Examiner disagrees. The objective of Kim is to deposit a film by ALE on a uniformly terminated surface. Marcus teaches the equivalence of uniform oxygen termination with uniform hydrogen termination.”

Apparently, the phrase “for removal of particles and native oxides” in Kim et al. carries no weight with the Examiner. However, Appellants still contend that

a plain reading of Kim et al. reveals that the purpose of the wet treatment and HF etching is “for removal of particles and native oxides”, and the result of the wet treatment and HF etching is a wafer surface that is “contamination-free and terminated with atomic hydrogen.”

***The Examiner has not explained the manner in which Kim et al.
would be terminated with oxygen instead of hydrogen.***

The Examiner seems to contend that it would be obvious to terminate the surface of the wafer of Kim et al. with oxygen instead of hydrogen. However, the Examiner completely fails to explain how this would be done. The hydrogen termination is a byproduct of the cleaning process of Kim et al. Appellants fail to see any disclosure in any of the cited references, including Marcus et al., which would motivate one of ordinary skill in the art to eliminate or modify the cleaning process of Kim et al. so as to avoid hydrogen termination. The Examiner has not addressed this point.

There is no teaching or suggestion in Marcus et al. or Luryi, individually or in combination, which would motivate one of ordinary skill in the art to modify the process of Kim et al. in the fashion suggested by the Examiner.

The Examiner further contends that Marcus et al. teaches the equivalence of hydrogen and oxygen termination. Even if this were true in the context of Marcus

et al., why exactly would one of ordinary skill eliminate or alter the cleaning step of Kim et al. to avoid hydrogen termination in favor of oxygen termination? How exactly would the wafer surface be cleaned without resultant hydrogen termination? What advantage would be gained? The Examiner has failed to address these issues.

The Marcus et al. reference does not teach the equivalence of hydrogen and oxygen termination in the context of Kim et al.

Also, any alleged equivalence between hydrogen and oxygen termination must taken in the context of the teachings of Marcus et al. as a whole. Marcus et al. is directed to a laser coating process, which is presented as an alternative to machine tool subtractive techniques. Attention is respectfully directed to the following passages of Marcus et al.:

“An alternative preferred embodiment of the present invention comprises a method and apparatus of nucleating and renucleating the gas-phase deposition of the desired phases that make up the solid freeform fabricated three-dimensional part. In particular, the alternative preferred embodiment allows for catalytic deposition of the patterned layers as a predefined target area. Target area is defined herein as the location in which energy beams transform material from a gas phase and deposits those materials onto an evolving part.” Col. 6, lines 40-49. (Emphasis added.)

Marcus et al. is directed to the use of an energy (laser) beam to selectively deposit material from its gas phase. Kim et al. is directed to atomic layer deposition (ALD) of Al_2O_3 films. (ALD is a technique in which deposition of each atomic layer of material is controlled by a pre-deposited layer of precursor, and in which precursors of various components of the film are introduced alternately.) One of ordinary skill would not be motivated to apply the laser coating techniques of Marcus et al. to the ALD technique of Kim et al.

Luryi would not motivate one of ordinary skill to modify Kim et al. to conduct an oxygen pre-flush treatment in the temperature range of claim 15.

As a separate matter, claim 15 recites termination of the substrate surface with oxygen atoms at a temperature of 120°C to 370°C . As explained in the present specification (page 10), this results in decomposition of radicals of the subsequently applied first reactant.

The Examiner's reliance on Luryi is misplaced with respect to the temperature range of claim 15. Luryi teaches that the surface of a porous substrate is intentionally oxidized in a cleaning process, prior to a later high temperature treatment which removes the oxide. However, Kim et al. aims to remove native oxides in the cleaning process thereof, and the teachings of Luryi would not

motivate on skilled in the art to oxidize the wafer surface of Kim et al. in the fashion apparently suggested by the Examiner.

For *at least* the reasons stated above, and for the reasons already of record, Applicants respectfully contend that Claims 15-18, 21-25 and 27 would not have been obvious to one of ordinary skill in art in view of the teachings of the cited references, taken individually or in combination.

B. 35 U.S.C. ¶103 – CLAIM 19

Claim 19 stands finally rejected under 35 U.S.C. ¶103 as being unpatentable over Kim et al. in view of Marcus et al. and Luryi and Comizzoli et al. However, Appellants respectfully contend that this rejection should be reversed for the same reason stated above regarding claims 15-18, 21-25 and 27.

C. CONCLUSION

For at least the reasons stated above, Appellant respectfully contends that the rejections of the appealed claims should all be reversed.

Respectfully submitted,

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Date: February 5, 2004

ATTACHMENT: Appendix – Appealed Claims

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APPENDIX – APPEALED CLAIMS

15. A method for forming an oxide film on the surface of a silicon substrate, comprising:

loading the substrate into a reaction chamber;

flushing the surface of the substrate with oxygen within the reaction chamber so as to uniformly terminate dangling bonds on the surface of the substrate with oxygen atoms at a substrate temperature of 120 to 370 °C;

chemically adsorbing a first reactant onto the terminated surface of the substrate by introducing the first reactant into the reaction chamber;

forming a film of an oxide material as a result of a chemical exchange or reaction of the chemically adsorbed first reactant and a second reactant by introducing the second reactant into the reaction chamber, wherein the oxide material includes of the oxygen atoms used to terminate the surface of the substrate.

16. The method of claim 15, further comprising removing from the chamber any of the first reactant physically adsorbed into the terminated substrate prior to introducing the second reactant into the reaction chamber.

17. The method of claim 15, wherein the thin oxide film is an aluminum oxide film.

18. The method of claim 17, wherein the first reactant is trimethylaluminum and the second reactant is water.

19. The method of claim 15, wherein an oxide material of the oxide film is one selected from the group consisting of TiO_2 , Ta_2O_5 , ZrO_2 , HfO_2 , Nb_2O_5 , CeO_2 , Y_2O_3 , SiO_2 , In_2O_3 , RuO_2 and IrO_2 .

20. *(withdrawn) The method of claim 15, wherein an oxide material of the oxide film is one selected from the group consisting of PbTiO_2 , SrRuO_3 , CaRuO_3 , $(\text{Ba},\text{Sr})\text{TiO}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$, $(\text{Sr},\text{Ca})\text{RuO}_3$, In_2O_3 doped with Sn, In_2O_3 doped with Fe, and In_2O_3 doped with Zr.*

21. The method of claim 15, further comprising removing an impurity layer adsorbed into or formed on the surface of the substrate before loading the substrate into the reaction chamber.

22. The method of claim 15, wherein an intermediate compound is generated upon introduction of the second reactant into the reaction chamber to form the oxide film, and wherein said method further comprises removing the intermediate compound from the reaction chamber.

23. The method of claim 18, wherein CH_4 is generated upon introduction of the water into the reaction chamber to form the aluminum oxide film, and wherein said method further comprises removing the CH_4 from the reaction chamber.

24. The method of claim 15, wherein the dangling bonds on the surface of the substrate are uniformly terminated by repeatedly injecting gas including the oxygen at least twice.

25. The method of claim 15, wherein the oxide film is a single atomic oxide film.

26. *(withdrawn) The method of claim 15, wherein the oxide film is a composite oxide film.*

27. The method of claim 15, wherein the substrate temperature is about 300°C .